



Carbon-coated graphite for anode of lithium ion rechargeable batteries: Carbon coating conditions and precursors

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ABSTRACT

Carbon coating of natural graphite particles was performed by mechanical mixing of natural graphite with different carbon precursors in a scale of about 100 g. Anode performance in lithium ion rechargeable batteries was studied on the resultant carbon-coated graphite. Carbon formed on graphite particles had amorphous structure and low density. By carbon coating, a decrease in irreversible capacity of the first charge/discharge cycle in an electrolyte solution of EC/PC = 3/1 was observed, without noticeable change in discharge capacity. Carbon derived from different precursors did not give any marked difference in anode performance of carbon-coated graphite. Optimum conditions for carbon coating were determined as the coating of 4–13 mass% at 700–1000 °C. The present mechanical mixing of natural graphite and carbon precursor in powder is concluded to be a simple but sufficient process to produce carbon-coated graphite for anode material in lithium ion rechargeable batteries. As carbon precursor, PVA was shown to be one of the appreciable carbon precursors.

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1. Introduction

Since lithium ion rechargeable batteries (LIBs) have been commercialized in the early 1990s, various carbonaceous materials have been applied as anode material, such as natural graphite, graphitic materials prepared from cokes, carbon fibers and meso-carbon microbeads, and also non-graphitic carbons derived from different resins [1–5]. Now, natural graphite is used in most of commercialized batteries mainly because of low cost, high capacity and stable charge/discharge performance. On the natural graphite flakes, carbon coating through various processes was proposed to improve the performance in LIBs [6–22], some of them being coupled with the formation of spherical particles, in addition to the dispersion of minute particles of some metals, such as Si [5,22] and Sn [23–25].

Carbon coating has been applied to various natural graphite flakes and spheres [6–9,11–19,21], and mesocarbon microbeads [10,20] by either chemical vapor deposition (CVD) under different conditions [6,8,9,12–15,17–19] or heat treatment of a mixture with an organic precursor at a temperature around 1000 °C under inert atmosphere [7,10,11,16,20,21]. Carbon coating was reported to be effective to reduce the irreversible capacity for the first

charge/discharge cycle and to improve the cyclability in ethylene carbonate (EC) electrolyte solution [6,8,11,13–19,21]. In addition, some papers reported that carbon-coated graphite can be used in electrolyte solutions contained propylene carbonate (PC) mixed with different solvents, EC [11], dimethylene carbonate (DMC) [9], EC and diethylene carbonate (DEC) [10,15], EC and DMC [16]. Polymer electrolyte was also used [7,20].

From industrial view point of the production of graphite materials for the anode of LIBs, carbon coating is attractive process to improve their performance. For carbon coating process, the heat treatment of the mixture of natural graphite with organic precursor is more interesting than CVD process, mainly because of cost performance of the production process. To prepare the mixture, two methods have been applied, mechanical mixing and impregnation through a solution of organic precursor. The former process is simpler than the latter to apply it to industrial production of anode material. However, many points have to be clarified for the industrialization of this carbon coating process through mechanical mixing of natural graphite and carbon precursor; the selection of substrate graphite and carbon precursor, mixing ratio of these two raw materials, heat treatment condition (temperature, holding period, heating program, etc.), heat treatment instrumental system for large scale production and so on. Recently, step-wise heating for carbon coating using poly(vinyl chloride) was reported to give better cyclability for anode graphite [21].

Therefore, a series of works on the production of graphite materials for the anode of LIBs were scheduled to clarify some problems

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mentioned above by taking into account of the expansion in the production scale to about 1000 kg in near future. In the present paper, thermoplastic carbon precursors, poly(vinyl alcohol) PVA and poly(vinyl chloride) PVC, were mainly used for carbon coating of a natural graphite of 100–300 g. On the resultant carbon-coated graphite samples, the anode performance was evaluated as the function of the amount of carbon, which was coated by changing the mixing ratio of PVA and PVC, and as that of the heat treatment temperature for carbon coating. In addition, various thermoplastic carbon precursors were also tested. Based on these experimental results, the optimum conditions for carbon coating and appropriate carbon precursor for the coating through mechanical mixing process were discussed.

2. Experimental

2.1. Carbon coating

As substrate graphite, natural graphite (NG) with an average size of 19 μm was selected. As precursor for carbon coating, different thermoplastic carbon precursors, poly(vinyl alcohol) PVA, poly(vinyl chloride) PVC, poly(vinyl pyrrolidone) PVP, poly(propylene) PP, high density poly(ethylene) HDPE, low density poly(ethylene) LDPE, poly(acryl amide) PAA and poly(ethylene terephthalate) PET, were used. All carbon precursors used were commercially available.

For detailed studies on the effect of carbon coating conditions on anode performance, carbon-coated graphite samples were prepared by using the precursors PVA and PVC. The powders of NG and either PVA or PVC were mixed in a rotary mixer with 1500 rpm for 3 min. Different mixing ratios of the precursor P_{mixed} were employed, which were 10–200 g per 100 g of graphite substrate, hereafter being expressed as 10–200 phg (per hundred grams of graphite). The powder mixture of 110–300 g (depending on the precursor content) was carbonized up to a temperature ranging from 700 to 1500 $^{\circ}\text{C}$ under N_2 flow. A heating rate to a programmed temperature was 10 $^{\circ}\text{C min}^{-1}$ and a flow rate of N_2 was 10 L min^{-1} . The mixture with P_{mixed} of PVA of 50 phg was heat-treated up to 2800 $^{\circ}\text{C}$ in Acheson-type furnace.

Other carbon precursors, PVP, PP, HDPE, LDPE, PAA and PET, were mixed with NG in P_{mixed} of 50 phg and then heat-treated at 900 $^{\circ}\text{C}$ with the same procedure as above.

2.2. Structure characterization

Morphology of the particles was observed under scanning electron microscope with an accelerating voltage of 15 kV. The amount of coated carbon C_{mixed} was calculated from the difference in weight of the sample mixture before and after heat treatment. Particle size

distribution was determined by using a laser diffraction technique and then average particle size was calculated. From the difference between average particle sizes before and after carbon coating, thickness of carbon layer coated was estimated.

Structure of carbon coated on graphite particles by using PVA was studied by measuring the following properties. Density of the powder was determined by immersion of butanol (immersion density D_{im}). Raman spectrum was measured on the powder with Ar laser (wavelength of 532 nm) and R -value, *i.e.*, intensity ratio of the band at 1360 cm^{-1} to that at 1580 cm^{-1} $I(1360)/I(1580)$, was determined as a parameter of graphitization degree. Surface area of the sample powder was calculated by BET method (S_{BET}) from adsorption isotherm of N_2 at 77 K. It has to be pointed out that these structural parameters, R -value and S_{BET} , measured on carbon-coated graphite samples were apparent values for the composites of highly crystallized natural graphite with low-crystallinity carbon derived from the carbonization of a thermoplastic precursor.

2.3. Electrochemical characterization

Carbon-coated graphite sample was mixed with poly(vinylidene fluoride) (PVdF) in 9:1 mass ratio using a 1-methyl-2-pyrrolidone solution of 12 mass% PVdF. The pasty solution dispersing sample powder was plated on a copper foil (40 mm \times 40 mm and about 100–120 μm thick) and then dried at 65 $^{\circ}\text{C}$ for more than 1 h and then at 135 $^{\circ}\text{C}$ for 5 h under vacuum. The sample sheet thus prepared was pressed to make the density of graphite sample in the sheet to be about 1.0 g cm^{-3} . On this sheet, the performance as an anode of LIB was determined at 25 $^{\circ}\text{C}$ by using three-electrode cell with counter and reference electrodes of lithium metal foils. The electrolyte used was 1 M LiClO_4 solution of ethylene carbonate EC with propylene carbonate PC in the ratio of 3/1 in volume. The battery was constructed in a glove box in argon atmosphere. Charge/discharge cycle was performed with a constant current density of 1.56 mA cm^{-2} (condition of 0.5C/0.5C) between 4 mV and 1.5 V at room temperature.

In the present work, main attention was paid to the first cycle of charge/discharge on carbon-coated graphite, because the merits of carbon coating on graphite were able to be understood from the data on the first cycle, *i.e.*, discharge capacity and irreversible capacity.

3. Results

3.1. Carbon coated

In Fig. 1, SEM images of the graphite samples after the heat treatment with different mixing ratios of PVA P_{mixed} at 900 $^{\circ}\text{C}$ are compared with that of the original graphite. By carbon coating

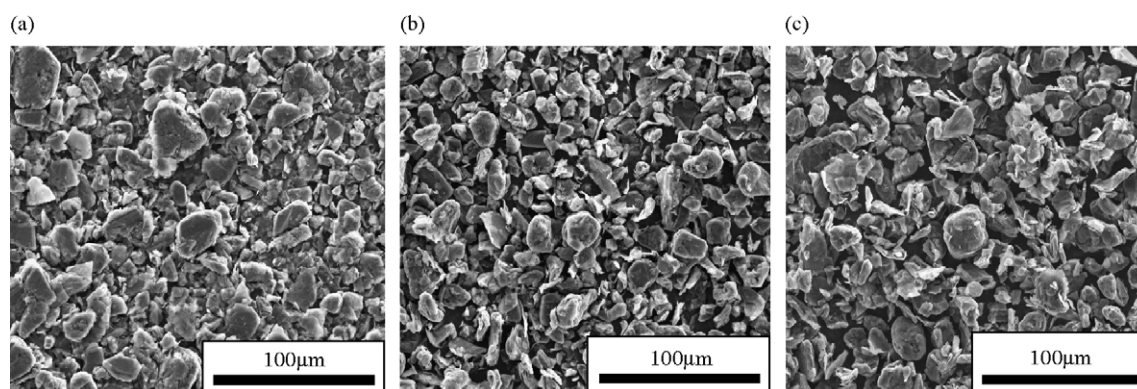


Fig. 1. SEM image of graphite before and after carbon coating process: (a) original NG; (b) from NG + 50 phg PVA; (c) from NG + 100 phg PVA.

process, morphology of the particles did not change appreciably from the original natural graphite and no marked coagulation of particles was observed. The samples prepared from the mixtures with P_{mixed} of either PVA or PVC of less than 50 phg were easily crushed by using fingers to pass through a sieve with an opening of the size of 63 μm . The samples from the mixtures with P_{mixed} of more than 50 phg were agglomerated, but they could pass through the sieve by gentle crushing on the mesh.

On the carbon-coated graphite samples prepared from the mixtures with different P_{mixed} of PVA up to 200 phg at 900 °C, particle size distribution was measured. As shown in three samples in Fig. 2a, the distribution shifts from the original to larger size with the increase in P_{mixed} . The difference in average particle size between the original graphite and the carbon-coated graphite is reasonably supposed to be due to carbon coating. The thickness of carbon layer estimated from this difference is plotted against amount of coated carbon C_{coated} in Fig. 2b. Although there is certain scattering of experimental points mainly due to the accuracy of carbon layer thickness, a linear relation can be assumed. This relation shows that it is reasonable to use the parameter C_{coated} as a measure of the thickness of carbon layer coated, the former being more reliable than the latter.

In Fig. 2c, relations between amount of carbon coated C_{coated} and mixing ratio P_{mixed} are shown for PVA and PVC after the carbonization at 900 °C. A good linear relation is obtained for PVA and PVC, showing a little higher carbonization yield of PVC than that of PVA (about 17 and 11 mass%, respectively).

Therefore, the amount of carbon coated C_{coated} was controlled by changing P_{mixed} of carbon precursor (PVA or PVC) from 10 to 200 phg and heat-treating at 900 °C, P_{mixed} of 100 phg giving the carbon residue of about 10 mass% from PVA and about 18 mass% from PVC.

In Fig. 3, dependences of three structural parameters, immersion density D_{im} , BET surface area S_{BET} and R -value, on amount of coated carbon C_{coated} are shown on carbon-coated graphite prepared with different P_{mixed} of PVA at 900 °C.

Immersion density D_{im} decreases linearly with increasing C_{coated} (Fig. 3a), although the original graphite does not coincide with the extrapolation of this linear relation to $C_{\text{coated}} = 0$. This result shows that the change in density of the sample powder with carbon coating is governed by coated carbon, which has very low density. Surface area S_{BET} decreases abruptly with a small increase in C_{coated} , up to 5 mass%, and then becomes almost constant (Fig. 3b). A further decrease in S_{BET} observed above 20 mass% C_{coated} is not sure because of so small surface area in comparison with the accuracy of its measurement. R -value, the intensity ratio of $I(1360)/I(1580)$ in Raman spectrum, is a parameter of the development of graphitic structure, the lower R -value suggesting the higher graphitization degree. In the present samples, R -value increases with increasing C_{coated} , suggesting that coated carbon has a high R -value, i.e., amorphous structure (Fig. 3c). The relation between R -value and C_{coated} can be also approximated to be linear, although its extrapolation to $C_{\text{coated}} = 0$ does not coincide with R -value measured on the original NG, suggesting that the change in R -value is mainly due to amorphous carbon coated on NG.

These experimental results show that the carbon coated on NG particles by using PVA as a carbon precursor is amorphous and has a low density. The amorphous carbon thus formed is supposed to fill the pores formed among NG crystals in a particle.

3.2. Effect of carbon coating on anode performance

3.2.1. Mixing ratio of carbon precursor

In Fig. 4, representative charge/discharge curves are shown on the original NG and carbon-coated NG, which was prepared from the mixture with P_{mixed} of PVA of 50 phg at 900 °C. No marked

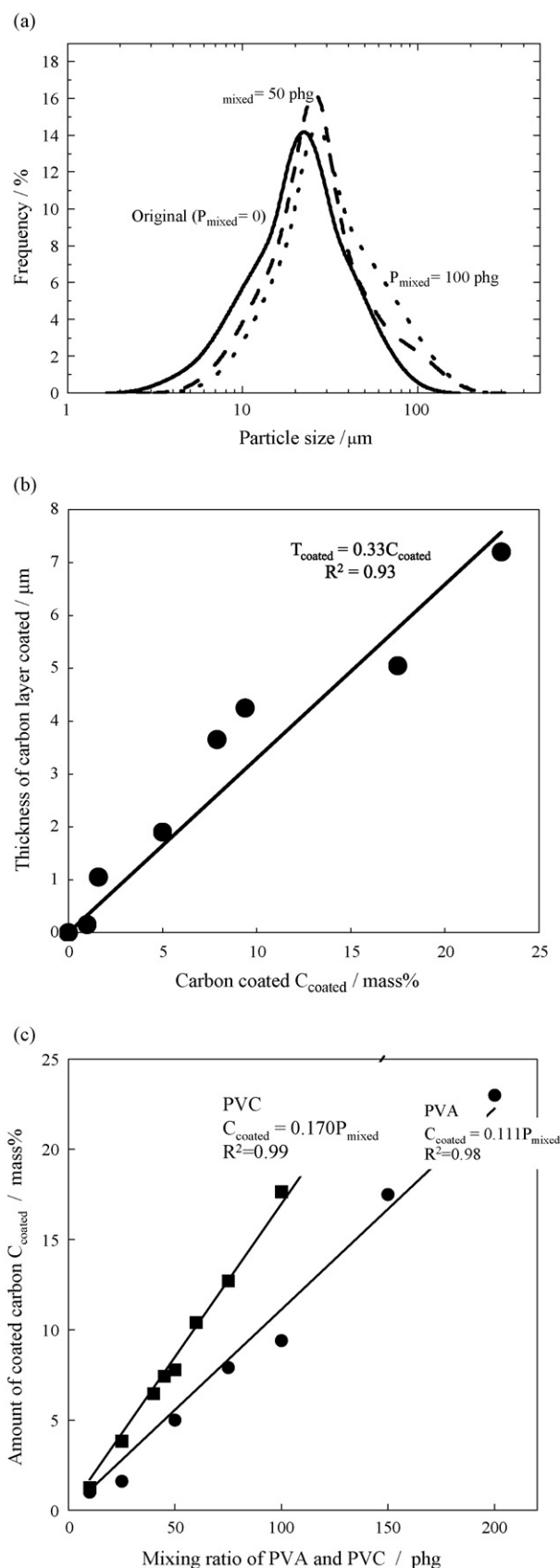


Fig. 2. Particle size distribution (a), relation between thickness of carbon layer and amount of coated carbon C_{coated} (b), and relation between C_{coated} and mixing ratio P_{mixed} of either PVA and PVC on carbon-coated graphite prepared at 900 °C.

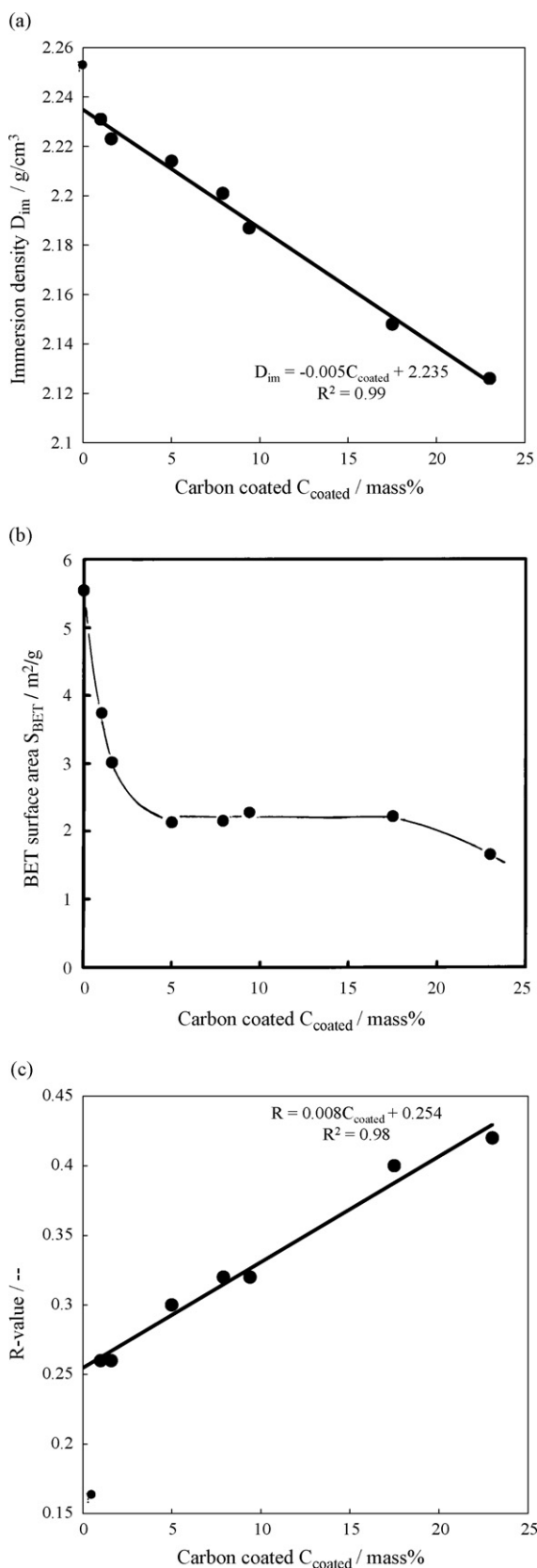


Fig. 3. Relations of immersion density D_{im} (a), BET surface area S_{BET} (b) and R-value measured from Raman spectrum (c) with amount of carbon coated C_{coated} on carbon-coated graphite prepared by using PVA at 900 °C.

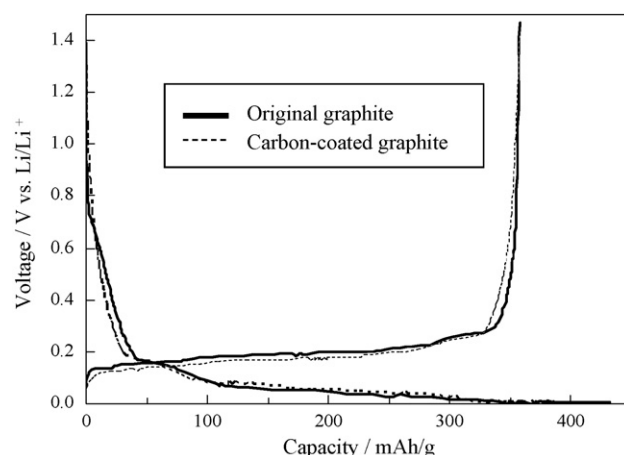


Fig. 4. Charge/discharge curves in 1 M LiClO₄ solution of EC/PC = 3/1 at 25 °C with a rate of 0.5C/0.5C for the original graphite and carbon-coated graphite prepared from the mixture with P_{mixed} of PVA of 50 phg at 900 °C.

change in the curves is observed, except the plateau due to the formation of solid/electrolyte interface seems to become slightly shorter after carbon coating.

In Fig. 5a, charge and discharge capacities measured with a charge/discharge rate of 0.5C/0.5C in 1 M LiClO₄ solution of EC/PC = 3/1 at 25 °C are plotted against mixing ratio P_{mixed} of PVA and PVC.

Charge capacity increases markedly by carbon coating in a range of P_{mixed} of 10–40 phg, but then decreases to show a plateau between 40 and 100 phg. Discharge capacity, which corresponds to reversible capacity observed on charge/discharge cycling, changes only a little with carbon coating, about 360 mAh g⁻¹. As a consequence of the changes in charge and discharge capacities in Fig. 5a, irreversible capacity of about 45 mAh g⁻¹ in the first charge/discharge cycle for most carbon-coated graphite samples is smaller than the original NG without carbon coating (75 mAh g⁻¹), except a high value for the samples obtained by using P_{mixed} of 10–40 phg on both PVA and PVC, as shown in Fig. 5b. Coulombic efficiency for the first charge/discharge cycle was about 82% for the original graphite and about 84–89% for the carbon-coated graphite prepared by P_{mixed} of 50–100 phg. In Fig. 5, the experimental points obtained by using PVA and PVC are not differentiated because the difference is mainly observed in the range of P_{mixed} of 10–40 phg, where undesirable high charge capacities and so high irreversible capacity are measured.

The experimental results obtained by changing P_{mixed} of PVA and PVC show that its range between 50 and 100 phg is preferable for getting an improvement in the performance of anode graphite, decrease in irreversible capacity from 75 to about 45 mAh g⁻¹ without any appreciable change in discharge capacity by the carbon coating of C_{coated} from 4 to 10 mass%.

3.2.2. Heat treatment temperature

Carbon-coated graphite samples were prepared from the mixture with P_{mixed} of 50 phg by the heat treatment at different temperatures from 700 to 1500 °C. Changes in charge and discharge capacities with heat treatment temperature HTT are shown in Fig. 6a, and that in irreversible capacity is shown in Fig. 6b. In Fig. 6, the experimental points for PVA and PVC are not differentiated above 1100 °C by the same reason as in Fig. 5.

As shown in Fig. 6a, charge capacity is almost constant for the carbon-coated graphite prepared at a temperature from 700 to 1000 °C, but becomes very high for the samples heat-treated above 1000 °C. At 1100 °C, carbon coating with PVA gives relatively high charge capacity, but that with PVC gives almost the same capacity as

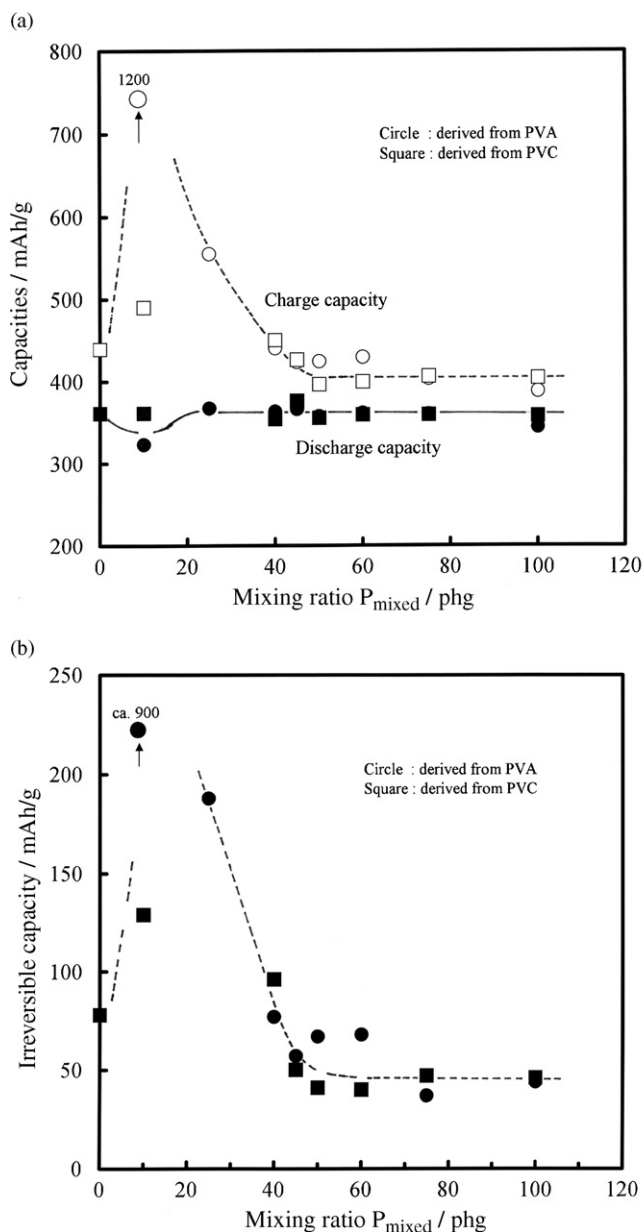


Fig. 5. Changes in charge, discharge (a) and irreversible (b) capacities with mixing ratio P_{mixed} on carbon-coated graphite prepared from the mixture with PVA and PVC at 900 °C.

lower temperatures, although both precursors give very high charge capacity above 1200 °C. Change in discharge capacity with HTT is very little between 700 and 1000 °C, tending to decrease slightly above 1000 °C. As a consequence, irreversible capacity increases rapidly above 1000 °C (Fig. 6b). In HTT range of 700–1000 °C, irreversible capacity becomes smaller than 75 mAh g⁻¹ for the original NG without carbon coating.

The present results on the effect of HTT shows that carbon coating process has to be done in a temperature range from 700 to 1000 °C. A high temperature heat treatment above 1300 °C, is not preferable, which results in high irreversible capacity.

3.3. Carbon precursors for carbon coating

Since certain relation was observed between estimated thickness of carbon layer coated and amount of coated carbon C_{coated} (Fig. 2b), these two parameters were measured on carbon-coated

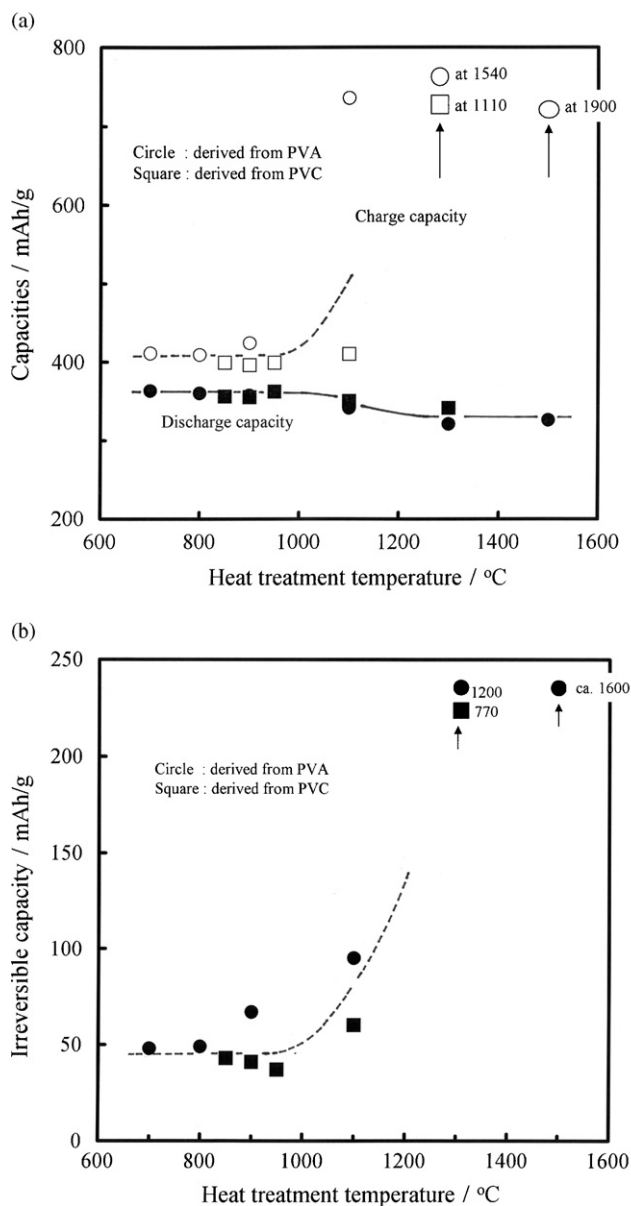


Fig. 6. Changes in charge, discharge (a) and irreversible (b) capacities with heat treatment temperature HTT on carbon-coated graphite prepared from the mixtures with a mixing ratio of 50 phg of PVA and PVC.

graphite samples prepared from the mixtures of NG with different carbon precursors in a constant mixing ratio P_{mixed} of 50 phg at 900 °C. The results are listed in Table 1.

On the basis of the results shown in Table 1, the thermoplastic resins used may be classified into the following three groups as the carbon precursor for carbon coating of graphite particles:

Group I Precursors giving low carbon residue, which are represented by poly(ethylene)'s (HDPE and LDPE) and poly(propylene) (PP). Carbon residue was less than

Table 1
Amount of coated carbon C_{coated} (carbon residue) and estimated thickness of carbon layer coated.

Carbon precursor	HDPE	LDPE	PP	PVA	PVC	PVP	PAA	PET
Carbon residue C_{coated} (mass%)	1.2	2.3	2.1	5.3	8.2	7.5	21.3	39.5
Estimated thickness of carbon layer (μm)	0.0	0.0	0.0	4.2	2.0	4.1	1.1	3.0

Table 2

Anode performance for the first charge/discharge cycle on carbon-coated graphite prepared from different thermoplastic carbon precursors.

Carbon precursor		Carbon coating condition	Capacity in first cycle (mAh g ⁻¹)		
			Charge	Discharge	Irreversible
Group I	HDPE	Mixing ratio of	1197	409	788
Group II	PVA	50 phg, at	424	357	67
	PVC	900 °C	396	355	41
	PVP		421	371	50
Group III	PVA+PVP		410	361	49
	PAA		425	347	78
	PVA+PAA		419	371	48
	PET		369	313	56
NG		No carbon coating	439	361	78

3 mass% and an estimated thickness of carbon layer was negligibly small.

Group II Precursors giving medium carbon residue, which are represented by poly(vinyl alcohol) (PVA), poly(vinyl chloride) (PVC) and poly(vinyl pyrrolidone) (PVP). Carbon residue was in a range from 4 to 11 mass% and an estimated thickness of carbon layer was more than 1 μm.

Group III Precursors giving high carbon residue, which are represented by poly(acryl amide) (PAA) and poly(ethylene terephthalate) (PET). Yield of carbon residue was more than 20 mass%, although an estimated thickness of carbon layer was more than 1 μm.

In Table 2, charge, discharge and irreversible capacities for the first cycle in the electrolyte solution of EC/PC = 3/1 with the rate of 0.5C/0.5C are listed on the carbon-coated graphite samples together with the original graphite. The samples were prepared by using P_{mixed} of 50 phg of different thermoplastic precursors at 900 °C. Two samples were prepared by using a mixture of two kinds of precursors, *i.e.*, mixtures of PVA with PVC and PVA with PAA.

The carbon-coated graphite samples prepared by using carbon precursors in Group II, PVA, PVC and PVP, give a little smaller charge capacity and almost the same discharge capacity, as a consequence smaller irreversible capacity, than the original graphite without carbon coating. Mixing of two precursors in Group II (PVA + PVP) seems no effect on anode performance. The carbon-coated graphite prepared by using precursors PAA and PET in Group III give a little

smaller discharge capacity than the original graphite, which is probably due to the fact that these precursors give a little larger amount of coated carbon than the optimum 10 mass%. By mixing of PVA (Group II) to PAA (Group III), anode performance seems to be recovered, comparable discharge and smaller irreversible capacities than the original graphite. The precursor HDPE in Group I gives very high charge and irreversible capacities, probably due to a small amount of carbon coating, less than 3 mass%.

4. Discussion

4.1. Carbon coated

In Fig. 7, immersion density D_{im} and R -value of carbon-coated graphite samples, which were prepared from the mixtures with different P_{mixed} 's of PVA at 900 °C and those with P_{mixed} of 50 phg at different HTTs, are plotted against amount of coated carbon C_{coated} . The samples prepared at different HTTs have almost the same value of C_{coated} , 5.0–5.3 mass%, and so HTT value is indicated for some of experimental points in the figures.

Density is lower for the sample prepared with the higher P_{mixed} , which is due to the coating by amorphous low-density carbon, and also at the higher HTT, which suggests that the density of coated carbon becomes high with increasing HTT. The matrix graphite has high crystallinity, *i.e.*, low R -value, but the coated carbon has low crystallinity, *i.e.*, high R -value, and R -value observed on the carbon-coated graphite samples is reasonably supposed to be a summation of the contribution from these two components. The increase in R with increasing C_{coated} is understood from the increase in the relative contribution from coated carbon due to the increase in the thickness of coated carbon. The decrease in R with HTT, much pronounced than that with C_{coated} , is due to the improvement in crystallinity of coated carbon. After the heat treatment at 2800 °C, R -value becomes smaller than the original NG without carbon coating, suggesting that the structural annealing of NG subjected under pulverization process before carbon coating occurs together with structural improvement in coated carbon at high temperature as 2800 °C.

4.2. Effect of coating conditions on anode performance

In Fig. 8a and b, changes in discharge and irreversible capacities with C_{coated} , respectively, are shown for carbon-coated graphite

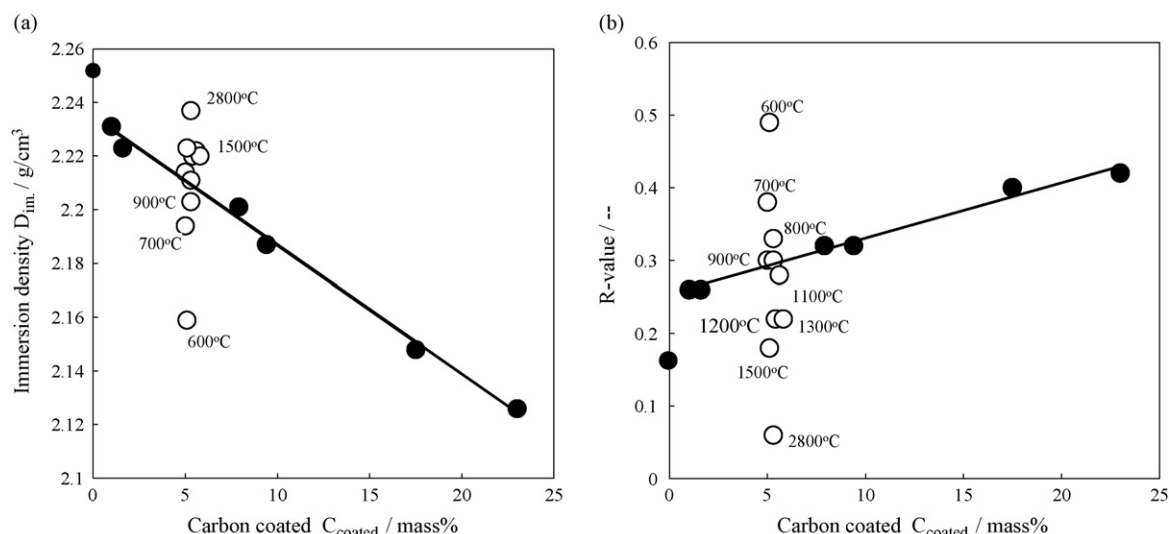


Fig. 7. Dependences of structural parameters, D_{im} (a) and R (b), on C_{coated} by changing P_{mixed} of PVA at 900 °C and by changing HTT.

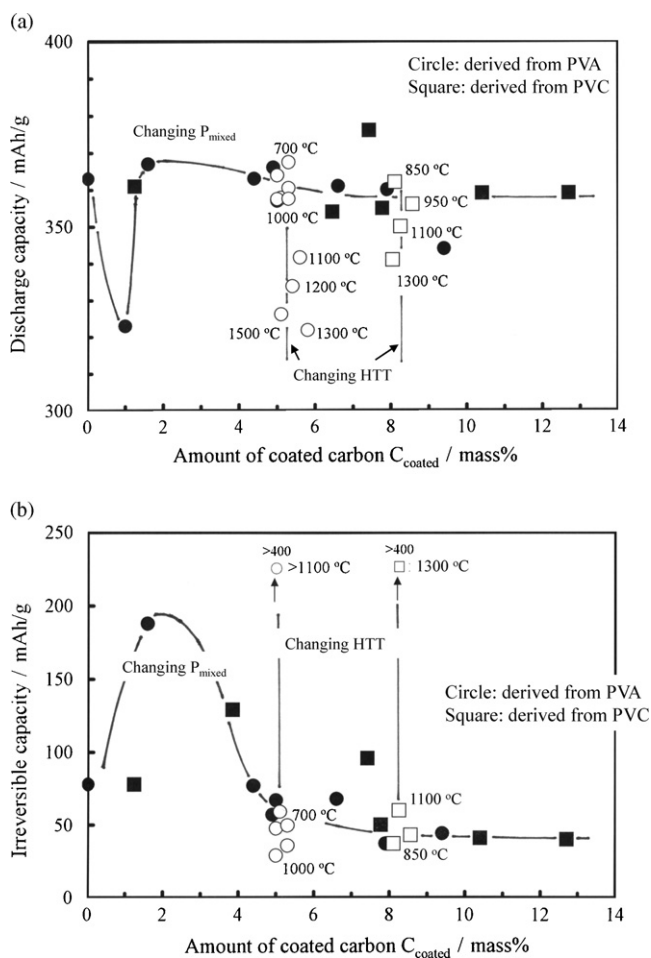


Fig. 8. Dependences of discharge (a) and irreversible (b) capacities on C_{coated} by changing P_{mixed} of either PVA or PVC at 900 °C and by changing HTT.

samples prepared by changing mixing ratio P_{mixed} of either PVA and PVC at 900 °C and also by changing heat treatment temperature on the mixtures of P_{mixed} of 50 phg.

Fig. 8a and b shows that C_{coated} and HTT have to be selected in order to have certain improvement in anode performance; C_{coated} in a range of 4–13 mass% and HTT in a range of 700–1000 °C are preferable. Carbon coating of about 1 mass% gives a low discharge capacity, lower than the original graphite by about 40 mAh g⁻¹, and that of 1–4 mass% gives a high irreversible capacity, a marked increase from 75 mAh g⁻¹ for the original graphite up to 190 mAh g⁻¹. Heat treatment at a temperature above 1000 °C results in an extremely high irreversible capacity, more than 400 mAh g⁻¹, although decrease in discharge capacity is not so remarkable, about 50 mAh g⁻¹ by the heat treatment at 1300 °C. By carbon coating in the range of 4–13 mass%, irreversible capacity decreases to a range of 50–30 mAh g⁻¹, much smaller than the original graphite (75 mAh g⁻¹), although discharge capacity is almost the same as the original (350 mAh g⁻¹).

Effect of HTT on anode performance was studied by using a P_{mixed} of 50 phg for PVA and PVC, which gave C_{coated} of about 5 and 8 mass%, because of different carbon yield from PVA and PVC (about 11 and 17 mass%, respectively). The sample prepared from PVA at 1100 °C has extremely high irreversible capacity, but that from PVC at the same temperature gives a low irreversible capacity, although discharge capacities for these two samples are almost the same. This experimental result suggests that effect of HTT can be changed by changing C_{coated} , though much detailed study is required.

In order to have discharge capacity comparable to and irreversible capacity smaller than the original graphite by carbon coating in the electrolyte solution of EC/PC = 3/1, the coating condition has to be limited; C_{coated} has to be 4–13 mass% and HTT to be in a range of 700–1000 °C.

5. Conclusions

Carbon coating of natural graphite particles was successfully performed by mechanical mixing of natural graphite with different carbon precursors. Carbon formed on graphite particles was characterized by amorphous structure and low density, and was impregnated into the pores among graphite crystals, which were concluded from the measurements of immersion density, Raman spectrum and BET surface area. By carbon coating, a decrease in irreversible capacity of the first charge/discharge cycle in LIB was confirmed in 1 M LiClO₄ solution of EC/PC = 3/1, without noticeable change in discharge capacity. From the view point of anode performance of carbon-coated graphite, carbon precursors are classified into three groups and the precursor represented by PVA and PVC (Group II) can give improvement in anode performance. Carbon derived from different precursors in Group II seemed not to give any noticeable difference in anode performance in the battery.

In order to have certain improvement in anode performance, optimum conditions for carbon coating had to be applied: the amount of coated carbon in the range of 4–13 mass% (mixing ratio of PVA and PVC of 40–100 phg) and heat treatment temperature in the range of 700–1000 °C.

From the consideration of industrial production of carbon-coated graphite for anode material of lithium ion rechargeable batteries, the present mechanical mixing of natural graphite and carbon precursor in powder has certain advantage in a simple preparation process, in comparison with other processes, *i.e.*, impregnation of carbon precursor and CVD of carbon. As carbon precursor, PVA is one of appreciable carbon precursors, but PVC is not recommended because of the evolution of chlorine-containing gases during heat treatment. PET might be also used as carbon precursor with much smaller mixing ratio than PVA, although detailed examination on the coating conditions is required. PVA has been successfully used for the carbon coating on MgO to prepare mesoporous carbon [26,27] and also on anatase-type TiO₂ to enhance its photocatalytic activity [28,29].

For practical application of this coating process, carbon precursor has to be selected from additional view points, such as price, available purity and particle size, stable supply, etc. In the present work, carbon-coated graphite was prepared in a scale of about 100 g per a batch. However, it has to be mentioned that the production in a scale of about 900 kg per batch was shown to be possible in the factory and the homogeneity in a batch was confirmed [30,31].

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